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cross-sections**

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Low temperature mid-infrared cross-sections for peroxyacetyl nitrate (PAN) vapour

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Laboratory absorption spectra of peroxyacetyl nitrate (PAN, $\text{CH}_3\text{C}(\text{O})\text{OONO}_2$) vapour have been measured in the mid-infrared range 550 cm^{-1} to 1400 cm^{-1} (18.2 to $7.14\text{ }\mu\text{m}$) at both 250 K and 273 K , using a Fourier transform infrared spectrometer at a nominal spectral resolution of 0.25 cm^{-1} (unapodised). In addition, the 1600 cm^{-1} to 2200 cm^{-1} (6.25 to $4.54\text{ }\mu\text{m}$) spectral region has been measured at 250 K . Cross-sectional data at each temperature, as well as integrated band intensities and peak infrared absorptivities for nine absorption bands of PAN in this spectral range, have been derived from a total of twelve separately measured PAN transmission spectra. A general increase in the peak absorption cross-section for all bands is noted with decreasing temperature, with cross-sectional increases in the range 6% (for the 1842 cm^{-1} band) and 30% (for the 991 cm^{-1} band) at 250 K , relative to those previously reported at 295 K . Differences in integrated band intensities range from -22% to $+16\%$ for the 1741 cm^{-1} and 991 cm^{-1} bands respectively over the same temperature range. These new absorption cross-sections for PAN are the first to be reported at temperatures below 295 K , allowing the possibility of improved retrievals of the atmospherically important PAN species from remotely sensed infrared spectra of the cold upper troposphere. These new cross-sectional data accompany this paper as an electronic supplement.

1. Introduction

PAN is one of the most important odd-nitrogen (NO_y) compounds in the atmosphere, both through its direct influence on the oxidising power of the atmosphere and also through its indirect role as a reservoir species for active nitrogen (Singh and Hanst, 1981; Singh, 1987). It is also a super greenhouse gas in its own right, although the impact of this remains to be studied. Furthermore, PAN has often been noted to be the most abundant NO_y species in the middle and upper troposphere in pollution events (Roberts, 1990; Roberts et al., 2004).

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PAN is formed in the atmosphere by organic photochemistry in the presence of NO₂ with an atmospheric lifetime dominated by thermolysis in the lower troposphere (<7 km) and photolysis in the upper troposphere (Talukdar et al., 1995). It is the relatively long lifetime (of the order of months) of PAN in the cold upper troposphere that makes this species an important global transport vehicle for NO₂. PAN concentrations as high as 650 pptv (at 10 km altitude) have been observed in pollution plumes such as those measured by Roberts et al. (2004) in Asian pollution outflow.

Current measurements of PAN are limited to in situ sampling during specialised campaigns such as those described by Emmons et al. (1997), with uncertainties of the order 30% at typical upper troposphere (UT) concentrations (Tanimoto et al., 1999). New satellite missions such as the infrared limb-sounding Michelson Interferometer for Passive Atmospheric Sounding (MIPAS) described by Fischer and Oelhaf (1996) and launched onboard Envisat in March 2002, could provide an alternative means to remotely detect trace organic species such as PAN by virtue of their characteristic infrared signature; and to determine global concentrations. The retrieval of concentration data from satellite-derived spectra requires, for purposes of radiative transfer calculations, accurate reference laboratory cross-sections for the target species, as well as for other compounds having influence in the relevant spectral window, measured at temperatures and pressures appropriate to the atmosphere.

In this paper, we report the first data for the infrared absorption cross-sections of PAN vapour recorded at temperatures below 291 K, complementing a room temperature dataset reported previously by Allen et al. (2005). These new spectral data for PAN will allow greater confidence in the identification and potentially the retrieval of PAN concentration information for the colder temperatures of the free and upper troposphere. Atmospheric detection limits for PAN by this method are yet to be ascribed due to the variability in the performance of different infrared instruments (e.g. instrument noise and atmospheric pathlength). These laboratory measurements will allow such instrument-specific studies to be undertaken in the future.

2. Experimental Method

PAN is a relatively heavy (141 amu) asymmetric top molecule with twenty-seven fundamental vibration modes, of which fifteen are expected to influence the 550 to 2200 cm^{-1} spectral region. Nominal band centres for PAN absorption bands used in this work are based on band assignments made by [Bruckmann and Willner \(1983\)](#). The strong 794 and 1163 cm^{-1} PAN bands are expected to be of key interest for remote-sensing applications given their strong spectral influence in these atmospheric window regions.

Spectra presented here were recorded using a Bruker IFS 120HR Fourier transform infrared (FTIR) spectrometer at the Molecular Spectroscopy Facility, Rutherford Appleton Laboratory, UK. A Fourier transform spectrometer is employed here for its ability to simultaneously measure the wide spectral range required for the broad absorption bands of PAN (typically greater than 40 cm^{-1}). An evacuated 26.1 cm path length glass absorption cell equipped with wedged potassium bromide windows was interfaced with a customised gas handling vacuum line. Further details of the experimental procedure and sample generation are given by [Allen et al. \(2005\)](#). A short description is provided here, highlighting aspects of relevance to these experiments.

A liquid nitrogen-cooled MCT detector (MCT-D360) was used, giving an excellent signal-to-noise ratio over the region of interest (typically better than 500:1 after co-addition at 1740.5 cm^{-1} and 450:1 at worst for the 794.0 cm^{-1} PAN band). Three overlapping spectral regions in the mid-infrared were measured using a 1 mm stop-aperture and appropriate optical and electronic filters. The use of optical and electronic filters covering a narrow spectral range improved the signal-to-noise ratio in the measured spectra. Together with a small stop aperture, these filters effectively removed the effects of detector non-linearity, noted to be a problem with MCT detectors ([Richardson et al., 1998](#)). Using this method, no evidence of such non-linearity was observed in any of the measurements reported in this work.

PAN samples were prepared by the nitration of peracetic acid in a synthesis based on that described by [Gaffney et al. \(1984\)](#) and were tested for purity (found to be greater

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than 99%) by gas chromatography. At the cold temperatures of these experiments, no spectral evidence of contamination was observed in any measurement, as expected from vapour pressure and sample stability considerations. A summary of the sample and measurement parameters is given in Table 1, with each measurement (50 co-added scans) requiring approximately six minutes. This time was sufficiently small so as to neglect thermal decomposition of the PAN sample (estimated to be less than 0.5% of sample). Sample emission was not expected at the cold temperatures of these experiments as confirmed by spectral measurement of PAN samples with the infrared source switched off. All spectra were recorded at an instrument resolution of 0.25 cm⁻¹ (where resolution is defined here as 0.9/maximum optical path difference) and apodised with the Norton-Beer strong function (Norton and Beer, 1976, 1977). Five PAN samples were measured over a pressure range of 0.19 to 0.41 mb at both 273 K and 250 K across the spectral range 550 to 1400 cm⁻¹, which is noted to be of major importance for remote-sensing applications. In addition, two PAN samples were measured in the 1600 to 2200 cm⁻¹ spectral region at 250 K to observe the interesting PAN bands centred at 1741 cm⁻¹ and 1842 cm⁻¹. The upper limit on the potential sample pressure at 250 K was due to the small saturation vapour pressure of PAN at this temperature (approximately 1.4 mb) expected from the relationship reported by Bruckmann and Willner (1983).

Transmission spectra were calculated by ratioing PAN sample spectra with the average of background spectra recorded immediately before and after each sample measurement. The limited pressure range studied has the advantage that PAN bands do not approach saturation (>40% transmission for the strong 1741 cm⁻¹ at 1.3 mb) at the pathlength used here, and measurements are not therefore expected to be subject to possible non-linearities in the Beer-Lambert law such as described by Chu et al. (1999) at high optical densities.

Resolution of rotational fine structure was not observed in any measurement made in this work. An initial comparison of measurements recorded at 0.25 cm⁻¹ and 0.03 cm⁻¹ spectral resolution did not yield any resolution of fine structure or differences in the ob-

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served absorption peak intensity. Therefore higher resolution measurements (greater than 0.05 cm^{-1}) were not attempted in this study due to concerns over the stability of the sample over longer measurement times (e.g. greater than 1 h at 0.05 cm^{-1} nominal resolution).

5 Sample pressure was monitored by cross-calibrated 10 Torr and 1000 Torr (full-scale) MKS Baratron 390 pressure gauges (1 Torr=1.33 mb) after prior calibration with a certified aneroid manometer. To avoid decomposition or detonation of the thermally unstable purified PAN sample, the Baratron gauges were operated at room temperature rather than at the nominal 313 K thermo-regulated operating temperature. The uncertainty in the measured pressure using this method was calculated to be less than 0.7% of full-scale for the 10 Torr gauge.

10 The cell was equipped with a thermally insulating jacket and cooled using thermo-regulated nitrogen-cooled liquid ethanol, pumped around the outer surfaces of the cell. Cell temperature was monitored by a series of eight platinum resistance (PT-100) thermometers, attached in thermal contact with the external walls of the absorption cell, giving a typical mean accuracy of better than 0.1 K.

3. Results

Using an error-weighted linear least squares regression to the measured absorbance as a function of sample pressure for each spectral point, absolute absorption cross-sections at each temperature were calculated from the Beer-Lambert law:

$$I_{\nu} = I_{0\nu} e^{-n\sigma_{\nu}x}, \quad (1)$$

20 where n is the target gas molecular number density (calculated assuming ideal gas behaviour), σ_{ν} is the absorption cross-section per molecule as a function of wavenumber, ν ; and x is the absorption cell path length. The $I_{\nu}/I_{0\nu}$ term defines the transmission spectrum calculated for each measurement. Similarly, integrated band intensities and peak infrared absorptivities were also calculated from error-weighted regression fits to

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the nominal PAN band area and peak absorbance as a function of pressure respectively. Such error weighting accounts for the small uncertainty due to the measurement accuracy of sample pressure and temperature as well as radiometric errors such as instrumental noise.

Integrated band intensities and peak infrared absorptivities are given in Table 2 at each temperature. Similar results for PAN at room temperature (295 K) from Allen et al. (2005) are also quoted for comparison. The error quoted refers to a two standard deviation uncertainty (95% confidence level) calculated from fit statistics to the regression as described in more detail by Allen et al. (2005). The addition of dry nitrogen gas to these samples up to a total cell pressure (PAN+N₂) of 500 mb resulted in no significant evidence of broadening of the PAN absorption bands studied in this spectral range and negligible change (<0.1%) in calculated band intensities and peak infrared absorptivities confirming similar findings by Tsalkani and Toupance (1989) at room temperature.

There is an observed increase in both peak absorptivity and integrated band intensity with decreasing temperature for all but the 1741 and 1842 cm⁻¹ bands, for which an increase in the peak absorptivity is accompanied by a decrease in the integrated band intensity. A maximum 30% and minimum 6% increase is seen at 250 K for the 991 cm⁻¹ and 1842 cm⁻¹ peak absorptivities respectively, relative to those reported at 295 K. Differences in integrated band intensity at 250 K range from +16% and -22% relative to those reported at 295 K for the 991 cm⁻¹ and 1741 cm⁻¹ bands respectively. The relative uncertainty (within the 95% confidence level) of the results reported in Table 2 ranges between 4% at best for the strong 794 cm⁻¹ PAN integrated band intensity and 22% at worst for the very weak 1055 cm⁻¹ peak absorptivity. The decrease in accuracy for weaker PAN bands is due to the increased uncertainty introduced by baseline noise relative to their weak spectral signatures. For the five strongest PAN absorption bands, relative uncertainty is calculated to be less than 5% at all temperatures. This uncertainty, although small, does allow for some overlap between values reported at different temperatures in Table 2.

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The calculated absorption cross-sections across the spectral range covered at each temperature, are plotted in Fig. 1. Differences in the structure of the 794, 1163, 1741 and 1842 cm^{-1} bands with decreasing temperature are illustrated in more detail in Fig. 2, with an observed narrowing of these bands seen to be most significant for the 1741 and 1842 cm^{-1} bands. The full-width at half-maximum (FWHM) of the 1741 cm^{-1} band is reduced from 20 cm^{-1} at 295 K to 16 cm^{-1} at 250 K, whilst for the 1842 cm^{-1} band, this is reduced from 26 cm^{-1} to 23 cm^{-1} . In addition, some difference in the structure of the P, Q and R branching of the 1741 cm^{-1} PAN band is evident with a sharpening of the associated Q branch and a difference in the relative intensities of the P and R branches with decreasing temperature. Furthermore, the 1842 cm^{-1} band shows a shift in the point of maximum band intensity to higher wavenumber with the observed band centre shifted by 1 cm^{-1} from 1841.5 cm^{-1} , at 295 K, to 1842.5 cm^{-1} at 250 K.

The calculated peak absorption cross-sections are given in Table 3, with a comparison to room temperature data from Allen et al. (2005). Peak cross-sectional increases with decreasing temperature are in the range between 6% (for the 1842 cm^{-1} PAN band) and 30% (for the 991 cm^{-1} PAN band) for all bands between 295 K and 250 K, reflecting the increases in peak infrared absorptivity discussed earlier. Again, the relative uncertainty is less than 5% for the five principal absorption bands in this spectral range at all temperatures studied, although there is the possibility for some overlap within this uncertainty between the peak cross-sections calculated at each temperature.

The observed narrowing of PAN absorption bands and the corresponding increase in peak infrared absorptivity with decreasing temperature for all bands is suggested to be predominantly due to changes in the thermal population distribution of rotational energy levels. Explanations of increases in integrated band strength with decreasing temperature for other heavy asymmetric top molecules, similar to those reported here for all but the 1741 and 1842 cm^{-1} PAN bands, include the effects of saturation of narrow lines (McDaniel et al., 1991) and contributions from temperature dependant an-

harmonicity terms to the band intensities (Yao and Overend, 1976; Wang et al., 2001). In our measurements, we are confident that the experimental conditions ensure that the former cannot occur due to the low optical densities observed, whereas resonance between the high density of ro-vibrational states giving rise to infrared absorption is certainly a possibility. The marked decrease (28%) in the 1742 cm^{-1} integrated band intensity between 295 and 250 K, and associated changes in the relative intensities of the P, Q and R branches, is consistent with an expected decrease in the population (at lower temperatures) of possible superimposed hot bands and combination bands.

Such subtleties of structure, together with differences in intensity could be important for accurate remote sensing of PAN in the colder atmosphere from infrared measurements of the atmosphere. Further measurements of PAN at temperatures between 200 K and 250 K would therefore be desirable, although challenging, requiring both long sample pathlengths and accurate measurement of PAN at very small sample pressures (due to low saturation vapour pressure).

4. Conclusions

Absorption cross-sections for PAN in the atmospherically important spectral range 550 to 1400 cm^{-1} at 273 K and 250 K have been calculated for the first time from ten spectra of independent PAN samples at a spectral resolution of 0.25 cm^{-1} . In addition, the 1600 to 2200 cm^{-1} spectral region has been surveyed at 250 K.

Peak infrared absorptivities for all PAN bands are seen to increase with decreasing temperature with corresponding cross-sectional increases in the range 6% (for the strong 1842 cm^{-1} PAN band) and 30% (for the weak 991 cm^{-1} PAN band) at 250 K relative to those calculated at 295 K (using previously reported data by Allen et al. (2005)). Furthermore, integrated band intensities are observed to increase for all but the 1741 and 1842 cm^{-1} PAN bands. Changes in integrated band intensities at 250 K relative to those at 295 K range from -22% (for the 1741 cm^{-1} band) to $+16\%$ for the 991 cm^{-1} band. Relative uncertainty is typically better than 5% for the strong PAN

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bands, although there is the possibility of overlap between all values calculated across this temperature range.

Structural differences in the principal PAN absorption bands are noted, with a marked narrowing of the 1741 and 1842 bands cm^{-1} with decreasing temperature. Also a sharpening of the 1742 cm^{-1} PAN band Q branch and a difference in the relative intensity of the P and R branches is also noted for this band. There is also evidence for a shift ($+1 \text{ cm}^{-1}$) in the point of peak intensity of the 1842 cm^{-1} band from 1841.5 cm^{-1} to 1842.5 cm^{-1} . No significant broadening of PAN bands was observed with the addition of dry nitrogen gas (up to 500 mb total pressure) to pure PAN samples.

In particular, the temperature dependence of the 794 and 1163 cm^{-1} PAN bands is of great importance in remote-sensing applications due to their varying spectral influences in these atmospheric window regions at the colder temperatures of the free and upper troposphere. The measurement of these bands at three temperatures (295 K, 273 K and 250 K) gives greater confidence in their temperature dependence.

These new cross-sections accompany this work as an electronic supplement (<http://www.atmos-chem-phys.org/acpd/5/5669/acpd-5-5669-sp.zip>) and complement PAN cross-sectional data at room temperature (295 K) previously reported by Allen et al. (2005), together allowing a more accurate investigation of PAN throughout the troposphere.

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Table 1. Sample and measurement parameters for recorded spectra employed in the calculation of infrared data for PAN.

Temp. / K	Filter passband / cm^{-1}	Sample Pressure / mb
273	550–1400	0.19, 0.37, 0.38, 0.39, 0.41
250	550–1400	0.34, 0.39, 0.40, 0.41, 0.41
	1600–2200	0.48, 1.30

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Table 2. Peak infrared absorptivities ($10^{-1} \mu\text{mol}^{-1} \text{ m}^{-1}$, log to base 10) and integrated intensities ($\text{atm}^{-1} \text{ cm}^{-2}$) for PAN vapour at 250, 273 and 295 K. Units refer to 1013.25 mb at the nominal temperature. *295 K data taken from work by Allen et al. (2005).

Band centre/ cm^{-1}	250 K		273 K		295 K*	
	Peak Abs.	Band Int.	Peak Abs.	Band Int.	Peak Abs.	Band Int.
606	1.89±0.36	39.0±3.0	1.81±0.33	35.9±2.6	1.55±0.12	34.2±1.4
794	13.44±0.86	272±11.0	13.20±0.80	252±9.0	11.40±1.0	241±6.0
930	1.80±0.17	36.2±2.9	1.72±0.26	34.1±2.5	1.46±0.12	32.2±1.2
991	1.34±0.12	23.4±2.1	1.24±0.21	21.5±1.6	1.03±0.08	20.1±0.8
1055	0.78±0.17	18.4±1.4	0.70±0.14	16.9±1.0	0.62±0.06	16.0±0.8
1163	16.77±1.02	401±20.0	15.90±0.96	370±17.0	14.60±1.0	356±8.0
1302	13.01±0.64	313±16.0	12.64±0.74	315±13	11.40±0.8	281±6.0
1741	33.53±1.64	419±9.0	-	-	30.20±3.0	537±10.0
1842	10.11±0.77	242±4.0	-	-	9.50±1.2	260±6.0

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Table 3. Peak infrared absorption cross-section ($\times 10^{-18} \text{ cm}^2 \text{ molecule}^{-1}$) at 250, 273 and 295 K for nine PAN absorption bands in the mid-infrared. Errors shown represent the two standard deviation uncertainty calculated from a Beer's law fit at the nominal band centre. *295 K data taken from work by Allen et al. (2005).

Band centre / cm^{-1}	295 K*	273 K	250 K
606	0.18 ± 0.02	0.21 ± 0.04	0.22 ± 0.04
794	0.95 ± 0.02	1.10 ± 0.07	1.12 ± 0.07
930	0.17 ± 0.01	0.20 ± 0.03	0.21 ± 0.03
991	0.10 ± 0.01	0.12 ± 0.02	0.13 ± 0.02
1055	0.08 ± 0.01	0.09 ± 0.02	0.10 ± 0.02
1163	1.21 ± 0.03	1.32 ± 0.08	1.39 ± 0.08
1302	0.92 ± 0.02	1.02 ± 0.06	1.05 ± 0.06
1741	2.39 ± 0.06	-	2.68 ± 0.13
1842	0.74 ± 0.03	-	0.79 ± 0.06

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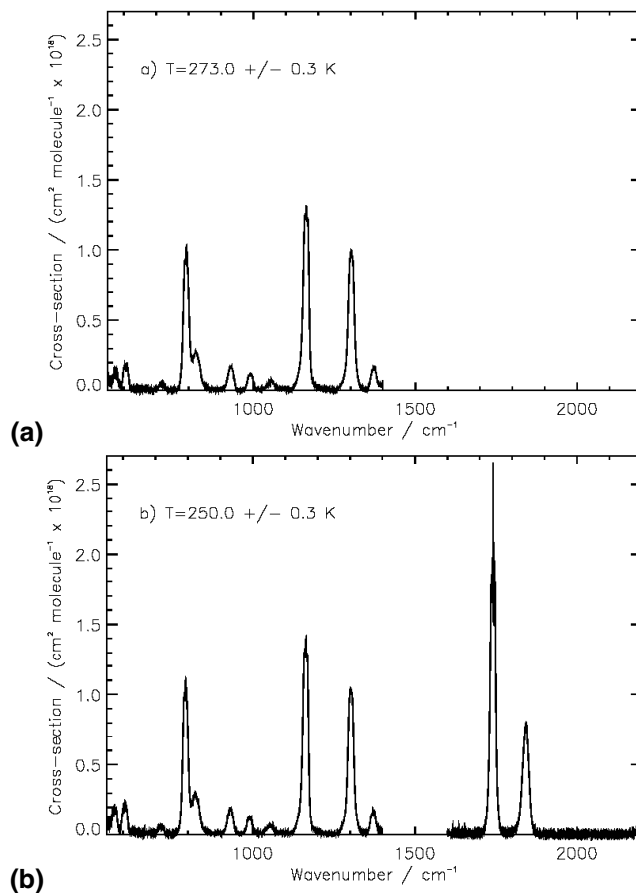


Fig. 1. PAN mid-infrared absorption cross-sections (0.25 cm⁻¹ resolution) at sample temperatures of: **(a)** 273 K±0.3 K (550 to 1400 cm⁻¹); and **(b)** 250±0.3 K (550–1400 cm⁻¹, 1600–2000 cm⁻¹).

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Low temperature PAN
cross-sections

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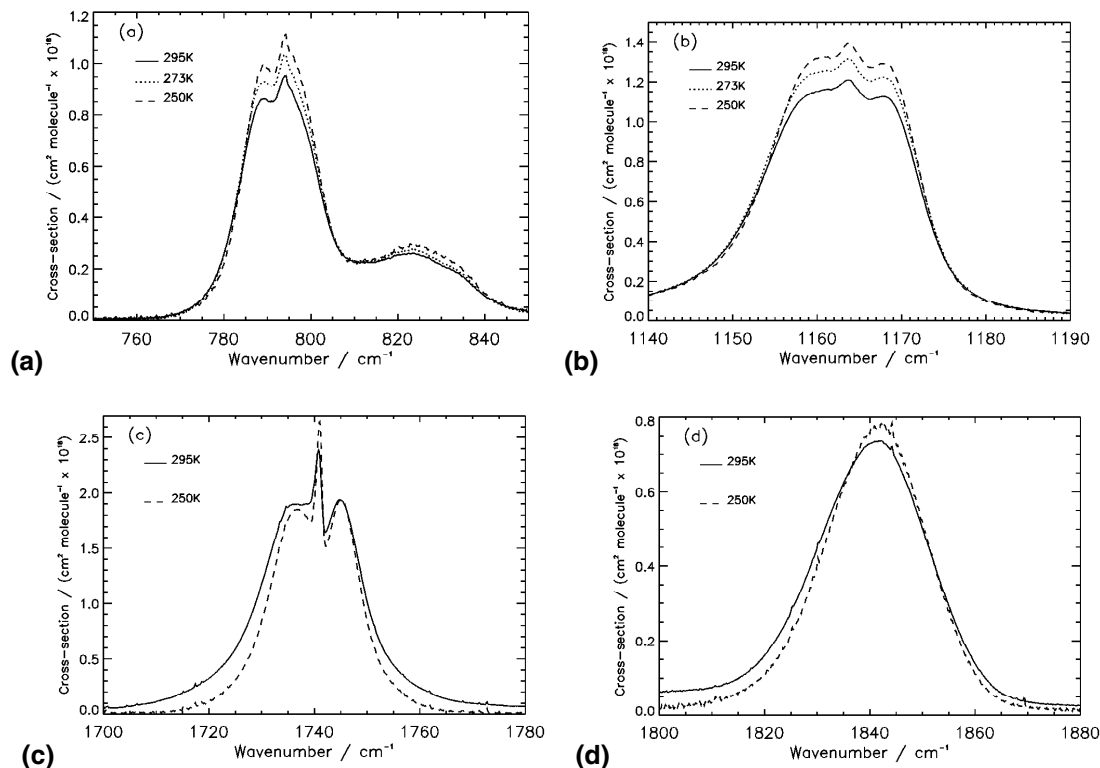


Fig. 2. A close up of the: (a) 794, (b) 1163, (c) 1741 and (d) 1842 cm⁻¹ PAN bands showing temperature dependence at 295 K (solid line) 273 K (dotted line) and 250 K (dashed line). Note: 295 K data taken from [Allen et al. \(2005\)](#).

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